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ZINC DUST CEMENTATION OF BISMUTH, CADMIUM, COBALT, COPPER, LEAD AND NICKEL FROM CHLORIDE SOLUTIONS

by

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ABSTRACT

Zinc dust cementation of Bi, Cd, Co, Cu, Pb and Ni from chloride solutions has been studied. The effects of the amount of added Zn dust, pH, temperature and the concentrations of HCl, NaCl and $ZnCl_2$ on the removal of these impurities from solution were determined. In the absence of NaCl and $ZnCl_2$, the rates of removal of these impurities from solution were Cu > Pb > Cd > Bi >> Ni > Co. The addition of NaCl to the solution substantially increased the cementation rate and the amount of Co and Ni cemented from solution, but slightly reduced the rates of Bi, Cd and Pb cementation. The presence of 50 g/L $ZnCl_2$ in solution had no significant effect on the cementation rate or on the amount of these metals removed from solution. The presence of Cu^{2+} in a solution containing Co or Ni enhanced the rate of removal of these species. After about 10 minutes, however, re-solution of the cemented Ni and Co occurred, even in the presence of excess Zn dust.

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CÉMENTATION PAR LA POUSSIÈRE DE ZINC DU BISMUTH, CADMIUM, COBALT, CUIVRE, PLOMB ET NICKEL À PARTIR DE SOLUTIONS DE CHLORURE

par

D.J. MacKinnon* et J.M. Brannen**

RÉSUMÉ

On a étudié la cémentation par la poussière de zinc du Bi, Cd, Co, Cu, Pb et Ni à partir de solutions de chlorure. Lors de ces études, on a déterminé les effets de la quantité de poussières de zinc ajoutée, du pH, de la température et des concentrations de HCl, NaCl et de $ZnCl_2$ sur l'extraction des impuretés contenus dans les solutions. En l'absence de NaCl et de $ZnCl_2$, le taux d'extraction des impuretés de la solution étaient Cu > Pb > Cd > Bi >> Ni > Co. L'addition de NaCl à la solution a augmenté considérablement le taux de cémentation ainsi que la quantité de Co et Ni cémentée, mais a légèrement réduit le taux de cémentation du Bi, Cd et Pb. La présence de 50 g/L de $ZnCl_2$ dans la solution n'a eu aucun effet significatif sur le taux d'extraction de ces éléments. Cependant, après environ 10 minutes, une nouvelle solution de Ni et de Co cémentés s'est produite même en présence de poussières de zinc en excès.

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INTRODUCTION

The treatment of complex sulphide ores using chloride processes eventually results in a zinc chloride electrolyte containing various metallic impurities. These impurities must be reduced to very low levels (<1 mg/L) to permit good quality zinc deposits to be electrowon at high current efficiency (>90%) (1). Cementation using zinc dust is one of the methods currently under investigation for purifying zinc chloride electrolyte.

Previous studies on the purification of $ZnCl_2$ electrolyte examined the cementation of Cu, Cd and Pb (2) and Co (3) using zinc dust. It was observed (2) that increasing $ZnCl_2$ concentration had no significant effect on the rate of Cu, Cd or Pb cementation; Cu, Cd and Pb were cemented from solution at about the same rate. The rate of Cu, Cd and Pb cementation from a solution containing 100 g/L $ZnCl_2$ increased with increasing amounts of Zn dust, reaching a maximum for 8 g/L Zn dust; the amount of excess Zn dust consumed was generally >5% but <8%.

The study of Co cementation on Zn dust from chloride solution (3) showed that the rate of Co cementation increased substantially with increasing temperature. The presence of Cu^{2+} in solution increased the initial rate of Co cementation; the presence of Pb^{2+} in solution reduced the rate of Co cementation as a result of the agglomeration of the particles into large isolated "balls". The rate of Co cementation increased significantly when the solution contained 3.0 M NaCl but decreased when the solution contained 30 g/L $ZnCl_2$.

Atkinson et al. (4) studied the purification of Cl_2-O_2 leach liquors by zinc cementation and observed that zinc dust addition to a leaching solution at 30°C decreased the Cd, Cu, Ni and Pb concentrations to acceptable levels of <3 mg/L each. Increasing the solution temperature to 75°C reduced

the Co level to <5 mg/L. Impurity removal rates from $ZnCl_2$ solutions were Pb > Cu = Cd > Ni >> Co.

In the present study, factors affecting the zinc dust cementation of Bi, Cd, Co, Cu, Pb and Ni, both singly and in various combinations, from chloride solutions were determined.

EXPERIMENTAL

The cementation reactions were carried out in a vessel containing 300 mL of the desired solution and fitted with a cover designed to hold and position a thermometer, a standard combination electrode and stirrer. The cover also contained an inlet for N_2 gas sparging and a sampling port from which solution was withdrawn at timed intervals for analysis by atomic absorption spectrophotometry. The reaction vessel was placed in a thermostated water bath to maintain the temperature constant, generally at 60°C.

The solutions consisted of various combinations of HCl (0.1-0.3 M), 3 M NaCl and 50 g/L $ZnCl_2$. The impurities were added either singly or in various combinations in the following concentrations: 2.0 g/L Cu, 1.0 g/L Pb, 0.4 g/L Ni, 0.2 g/L Cd, 0.2 g/L Co and 0.1 g/L Bi. Reaction was initiated by adding the desired amount of Zn dust (-70 + 43um) to the hot solution.

RESULTS AND DISCUSSION

COPPER

The cementation of copper using 4.0 g Zn dust at 60°C and a stirring rate of 250 RPM from solutions containing 0.1 M HCl, 0.1 M HCl + 3.0 M HCl, and 0.1 M HCl + 50 g/L $ZnCl_2$ is shown in Figure 1. All the copper was removed from solution after 5 minutes and the solution composition had an effect on the initial rate of Cu removal. The initial cementation rates were calculated from the linear portions of the plots shown in Figure 1. The fastest initial cementation rate (1.7 g/L/min) was obtained for the 0.1 M HCl + 3.0 M NaCl solution. The initial copper cementation rate in the presence of $ZnCl_2$ was similar to that obtained for a $ZnCl_2$-free solution; i.e., 1.0 g/L/min.

During the course of copper cementation, the solution pH increased gradually from 1.4 to 5.0 and 1.6 to 4.0 for the 0.1 M HCl and 0.1 M HCl + 50 g/L $ZnCl_2$ solutions, respectively. In the 0.1 M HCl + 3.0 M NaCl solution, the pH increased rapidly from 0.9 to 5.0 during the first 5 minutes and then remained constant.

COBALT AND NICKEL

The impurities Co and Ni were very similar in their behaviour toward zinc dust cementation and hence will be discussed together. The results obtained for Co and Ni cementation from the various solutions using 4.0 g Zn dust, 60°C and a 1000 RPM stirring rate are summarized in Figures 2 and 3, respectively. As these plots indicate, in HCl solution, the rates of Co and Ni cementation were very slow with the Co cementation rate being slower than that for Ni. The presence of 50 g/L $ZnCl_2$ further decreased the rate of Co cementation whereas that for Ni was slightly increased.

The presence of 3.0 M NaCl or 2 g/L Cu^{2+} in the solution resulted in a rapid increase in the Co and Ni cementation rates. This rapid cementation rate prevailed for about 3 minutes during which >70% of the Co and Ni were cemented from solution. Thereafter, the cementation rate slowed considerably. For the NaCl-containing solution, all the Co was removed after 30 minutes, whereas ~10% Ni still remained in solution after 40 minutes.

For the Cu^{2+}-containing solution, however, after about 10 minutes, re-solution of Co and Ni occurred with the rate of Co re-solution being greater than that for Ni.

In the presence of 3.0 M NaCl, variation of the initial solution pH between 1 and 3 had no significant effect on the initial rate of Ni cementation. Thus, both the effects of temperature and the amount of added zinc dust on the initial rate of Ni cementation were studied at pH 2.

The initial rate of Ni cementation was determined at 50, 60, 70 and 80°C using a solution containing 0.4 g/L Ni^{2+}, 3.0 M NaCl, initial pH 2.0, stirring rate 1000 RPM and 4.0 g Zn dust. The results are shown in Figure 4 in the form of an Arrhenius plot which gives an apparent activation energy of 31.0 kJ/mole. This is in good agreement with the value 31.8 kJ/mole obtained by plotting the data of Atkinson et al. (4), Table 1.

A previous study on cobalt cementation from chloride solution using zinc dust gave an activation energy of 79.5 kJ/mole in the presence of activators such as Pb and Cu ions (3). Again, this value is in fair agreement with that obtained from the data of Atkinson et al. (4); i.e., 55.1 kJ/mole, Table 1. Activation energies for Cu, Cd and Pb

cementation from chloride solutions using zinc dust were also calculated from the data of Atkinson et al. (4) and are summarized in Table 1. These data indicate that whereas Co and Ni cementation are chemically controlled reactions, the cementation of Cu, Cd and Pb are diffusionally-controlled processes under these experimental conditions.

The effect of the amount of added Zn dust on the initial rate of Ni cementation was determined at 70°C using a solution containing 0.4 g/L Ni, 3.0 M NaCl, pH 2.0 and stirring rate 1000 RPM. The results are shown in Figure 5 as a plot of initial Ni cementation rate vs the amount of added Zn dust. The initial rate of Ni cementation increases linearly with increasing Zn dust under these experimental conditions.

BISMUTH, CADMIUM AND LEAD

The results obtained for the cementation of Bi, Cd and Pb from various chloride solutions using zinc dust are summarized in Figures 6, 7 and 8, respectively. All three impurities showed similar behaviour with respect to variations in acid, $ZnCl_2$ and NaCl concentrations. In contrast to Cu, Co and Ni cementation, the presence of 3.0 M NaCl resulted in a slower rate of removal of Bi, Cd and Pb from solution as compared to the NaCl-free solutions. This behaviour may be related to the fact that the cementation of Bi, Cd and Pb was characterized by the agglomeration of the particles into numerous spherical "balls". The number of "balls" formed was dependent on the solution composition. In solutions containing NaCl, fewer but larger "balls" were formed and this resulted in a slower overall rate of cementation.

In a previous study on cadmium cementation from chloride solution using Zn dust (2), spherical agglomeration of the cement product was also observed. The number of "balls" formed was found to be dependent on the

Table 1. Activation energies for the cementation of metals on zinc from $ZnCl_2$ solutions calculated from the data of Adkinson et al. (4)

Metal	Activation Energy (kJ/mole)
Cu	15.9
Cd	15.9
Co	55.2
Ni	31.8
Pb	10.0

Temperature Range 30-75°C; 500 RPM; 4.0 g Zn dust

pH; e.g., at pH 5, 2 "balls" formed whereas at pH 3, 10 "balls" formed and the cementation rate was increased. Blaser and O'Keefe (5) observed a similar behavior for cadmium cementation on zinc dust from $ZnSO_4$ solutions. An SEM examination of the "balled" deposit revealed a morphology consisting of two-dimensional dendrites which results in the particles "locking" together (5).

As was the case in the previous studies (2,5), it was also observed in the current work that the presence of Cu^{2+} in the solution greatly accelerated the rate of cadmium cementation and also eliminated "balling" or agglomeration of the particles. An SEM examination of the "non-balled" deposit revealed that it consisted of a fine-grained, more massive morphology without dendritic trunks or branches and less excessive outward to lateral growth (5).

COMBINED IMPURITIES

The following solutions, 0.2 M HCl, 0.2 M HCl + 3.0 M NaCl, 0.2 M HCl + 50 g/L $ZnCl_2$ and 0.2 M HCl + 3.0 M NaCl + 50 g/L $ZnCl_2$ each containing 2.0 g/L Cu, 1.0 g/L Pb, 0.4 g/L Ni, 0.2 g/L Cd, 0.2 g/L Co and 0.1 g/L Bi were prepared and subjected to Zn dust cementation using 4.0 g Zn dust at 60°C and 1000 RPM for 50 minutes. The results are summarized in Table 2 in terms of percent metal cemented after 50 minutes. As indicated in Table 2, the only solution from which 100% of all impurities was cemented was that containing 0.2 M HCl + 3.0 MNaCl + 50 g/L $ZnCl_2$ In fact, all impurity metals were completely removed from this solution after 4 minutes. The only metals completely removed from all four solutions were Bi and Cu. In all other cases, re-solution or incomplete cementation of one or more of the impurities were observed. The impurities most prone

Table 2. Percent impurities cemented from various chloride solutions containing the combined impurities

Solution Composition	Percent Metal Cemented					
	Bi	Cd	Co	Cu	Pb	Ni
0.2 M HCl	100	71	25	100	100	100
0.2 M HCl + 3.0 M NaCl	100	53	47	100	92	100
0.2 M HCl + 50 g/L $ZnCl_2$	100	40	10	100	100	95
0.2 M HCl + 3.0 M NaCl + 50 g/L $ZnCl_2$	100	100	100	100	100	100

4.0 g Zn^o; 1000 RPM; 60°C; 50 minutes

to re-solution or incomplete cementation were cadmium and cobalt. The cementation plots for Cd and Co are shown in Figures 9 and 10, respectively.

As noted in Figure 9, the initial rate of Cd cementation from all four solutions was very rapid. With the exception of the 0.2 M HCl + 3.0 M NaCl solution, the Cd concentration became virtually zero after <3 minutes reaction time. For the 0.2 M HCl solution, re-solution of cadmium began to occur after about 25 minutes and gradually increased with time. For the 0.2 M HCl + 50 g/L $ZnCl_2$ solution, the cadmium began to redissolve after about 2 minutes, increasing rapidly to 0.1 g/L at 10 minutes and thereafter remaining constant. For the solution containing 0.2 M HCl + 3.0 M NaCl, the Cd concentration reached a minimum level of ~0.05 g/L after 1 minute reaction time and then increased slightly over the remainder of the experiment.

Re-solution of cadmium was not observed in the experiments in which the test solutions contained only cadmium or cadmium in combination with copper or lead. Atkinson et al. (4), however, observed that cadmium re-solution was a function of temperature with the degree of re-solution increasing with increasing temperature.

Cobalt (Figure 10), unlike cadmium, did not undergo re-solution but rather did not completely cement from some of the solutions tested. For the 0.2 M HCl + 3.0 M NaCl + 50 g/L $ZnCl_2$ solution, complete cementation of Co was achieved after 3 minutes, Figure 10. For the solution containing 0.2 M HCl + 3.0 M NaCl, initial Co cementation was rapid, decreasing to ~0.08 g/L after 1 minute; however, the Co concentration remained at about this level for the duration of the test. Cobalt removal from 0.2 M HCl solution reached a maximum of 0.06 g/L after about 15 minutes and remained constant thereafter. The least cobalt was cemented from the 0.2 M HCl + 50 g/L $ZnCl_2$ solution.

CONCLUSIONS

The cementation of bismuth, cadmium, cobalt, copper, lead and nickel from various chloride solutions using zinc dust has been studied. In HCl solution, the rate of removal of these impurities was in the order Cu > Pb > Cd > Bi >> Ni > Co. The addition of NaCl to the solution greatly increases the rates of Ni and Co cementation and slightly decreased the rates of Bi, Cd and Pb cementation. The presence of 50 g/L $ZnCl_2$ in the solution had no significant effect on the cementation rate or on the amount of these species removed from solution. Although the presence of Cu^{2+} in the solution enhanced the rates of Co and Ni cementation, re-solution of these species occurred after about 10 minutes of reaction.

One hundred percent of the combined impurities was cemented from the 0.2 M HCl + 3.0 M NaCl + 50 g/L $ZnCl_2$ solution after 4 minutes. This solution is suitable for Zn recovery by electrowinning. In the other chloride solutions used in this study, cadmium was found to undergo re-solution and cobalt cementation was incomplete. These solutions would require an additional purification step prior to zinc electrowinning. Only bismuth and copper were completely cemented from all the solutions studied.

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FIGURE CAPTIONS

Fig. 1 - Plots showing the decrease in copper concentration as a function of time for various chloride solutions.

Fig. 2 - Plots showing the decrease in cobalt concentration as a function of time for various chloride solutions.

Fig. 3 - Plots showing the decrease in nickel concentration as a function of time for various chloride solutions.

Fig. 4 - Arrhenius plot for nickel cementation on Zn dust from 3.0 M NaCl solution at pH 2.

Fig. 5 - Plot showing the effect of the amount of added Zn dust on the initial rate of nickel cementation from 3.0 M NaCl solution at pH 2.

Fig. 6 - Plots showing the decrease in bismuth concentration as a function of time for various chloride solutions.

Fig. 7 - Plots showing the decrease in cadmium cementation as a function of time for various chloride solutions.

Fig. 8 - Plots showing the decrease in lead concentration as a function of time for various chloride solutions.

Fig. 9 - Plots showing the change in cadmium concentration as a function of time for various chloride solutions containing the combined impurities.

Fig. 10 - Plots showing the change in cobalt concentration as a function of time for various chloride solutions containing the combined impurities.

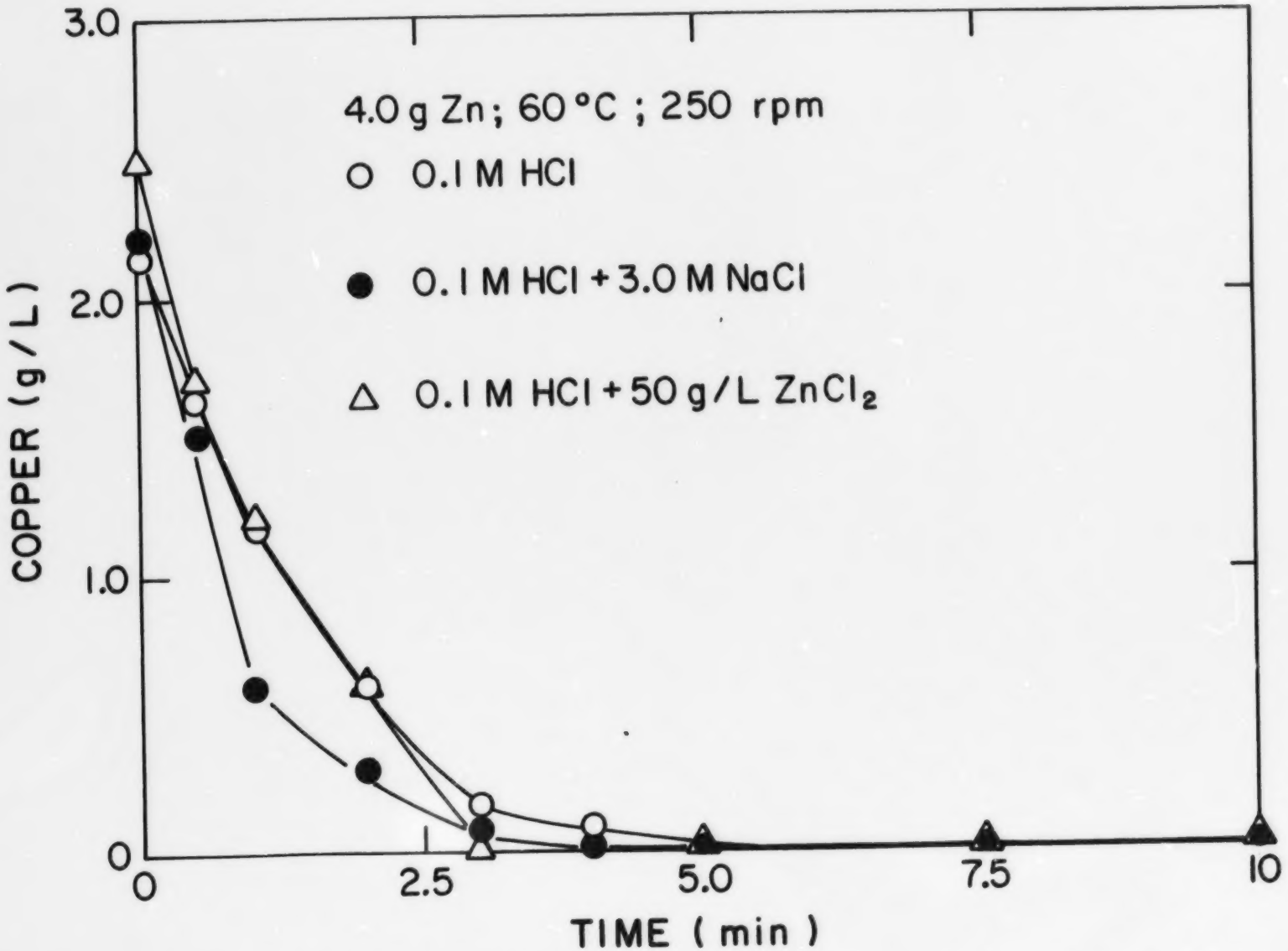

Fig. 1 - Plots showing the decrease in copper concentration as a function of time for various chloride solutions

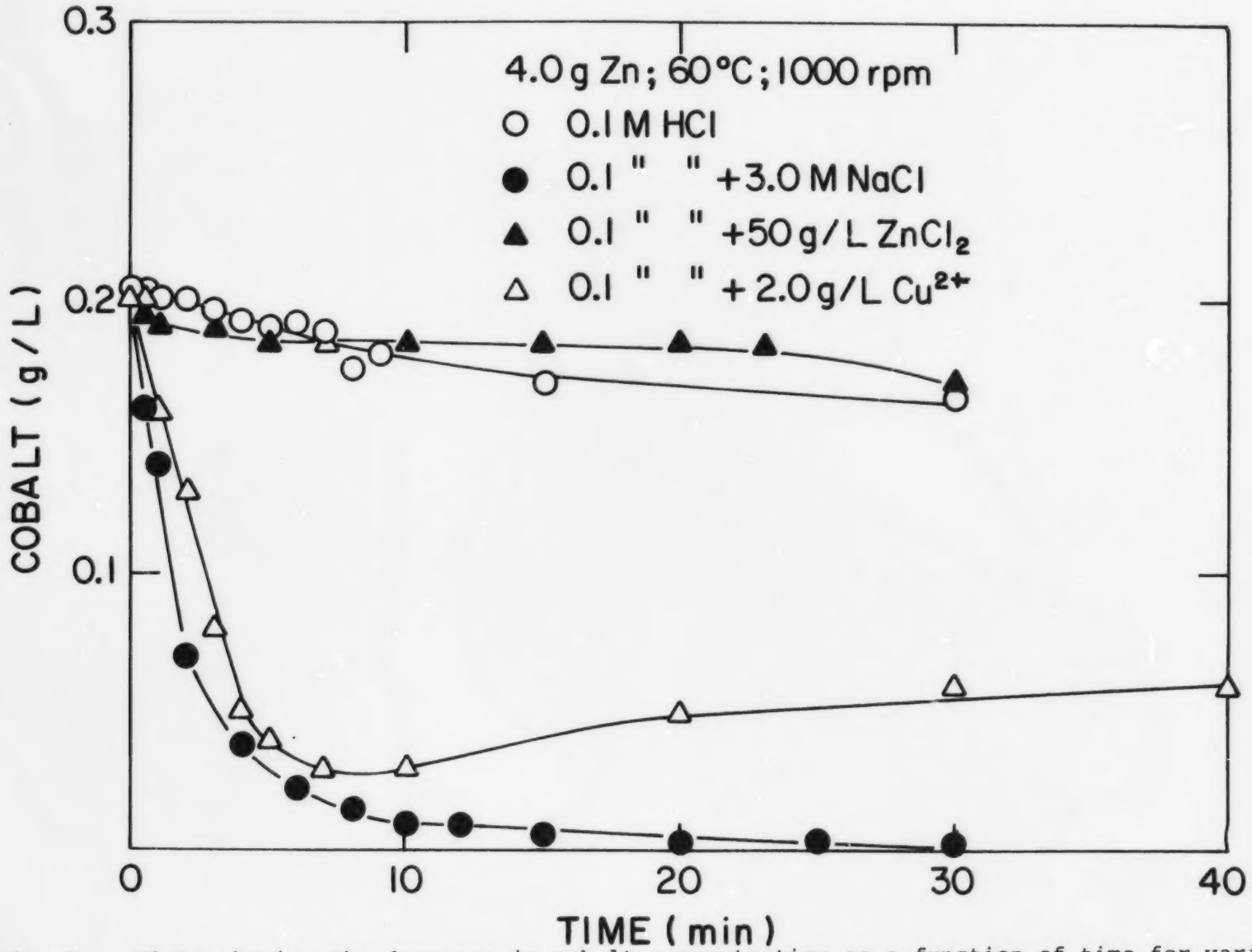

Fig. 2 - Plots showing the decrease in cobalt concentration as a function of time for various chloride solutions.

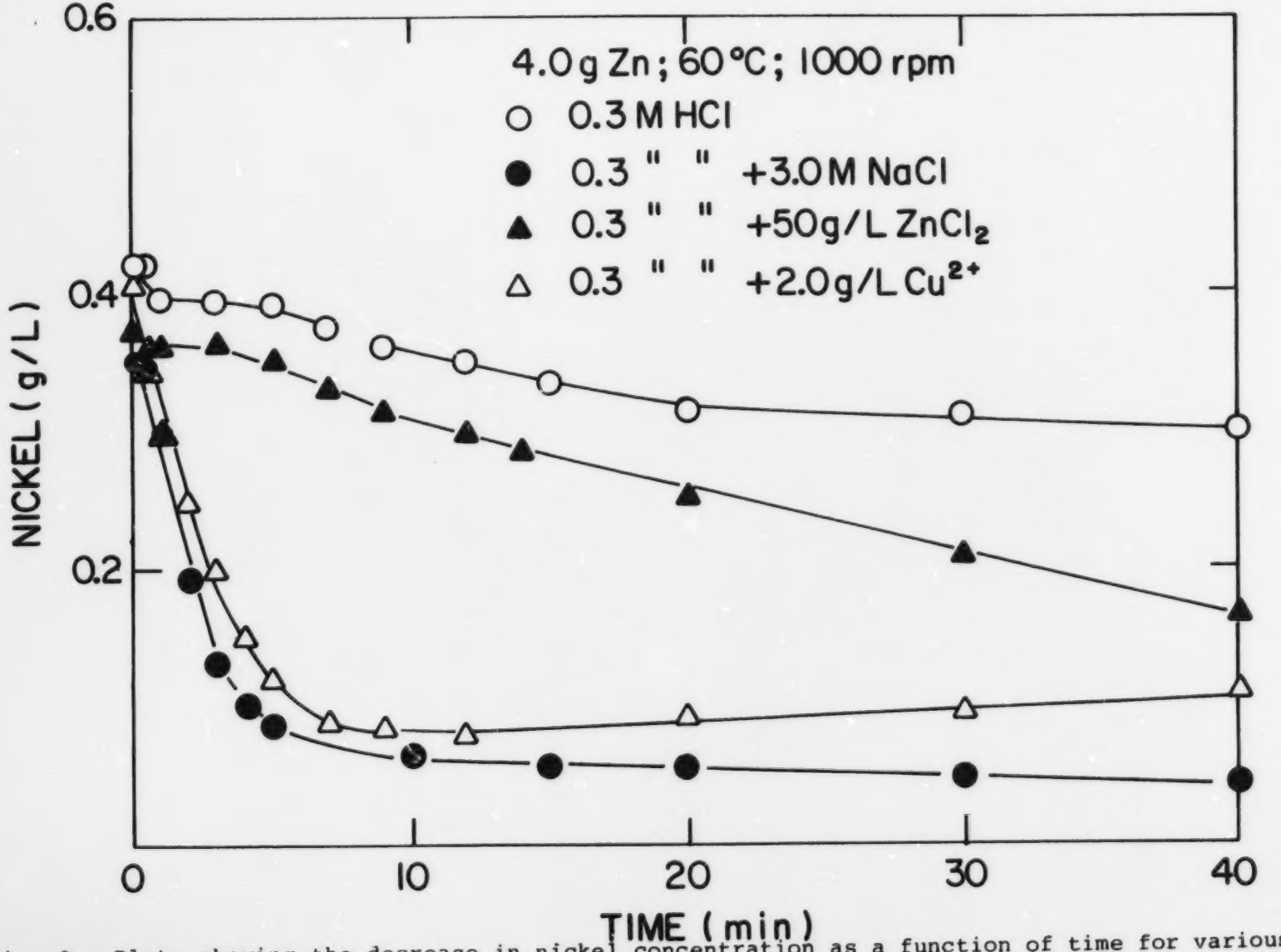

Fig. 3 - Plots showing the decrease in nickel concentration as a function of time for various chloride solutions.

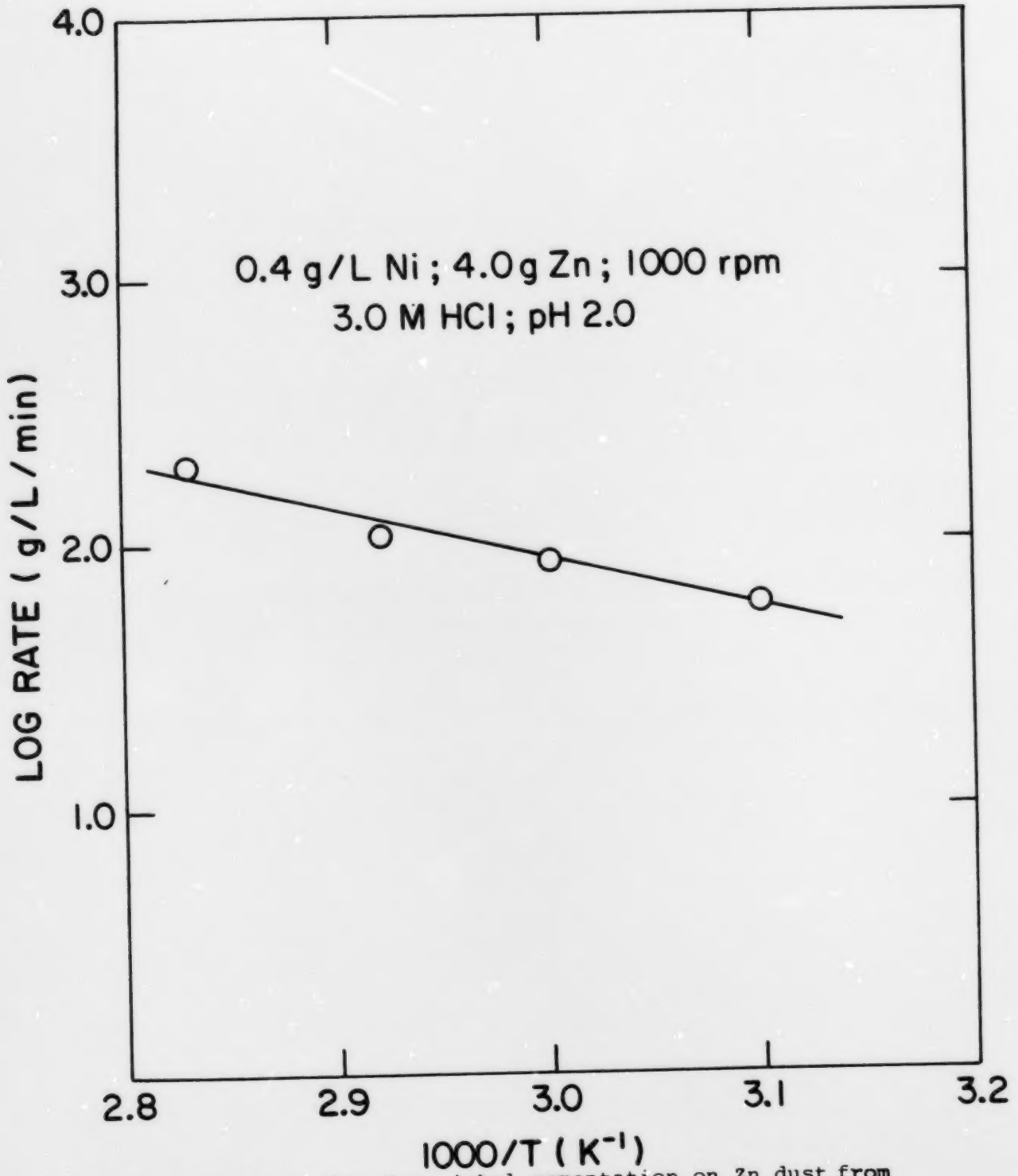

Fig. 4 - Arrhenius plot for nickel cementation on Zn dust from 3.0 M NaCl solution at pH 2.

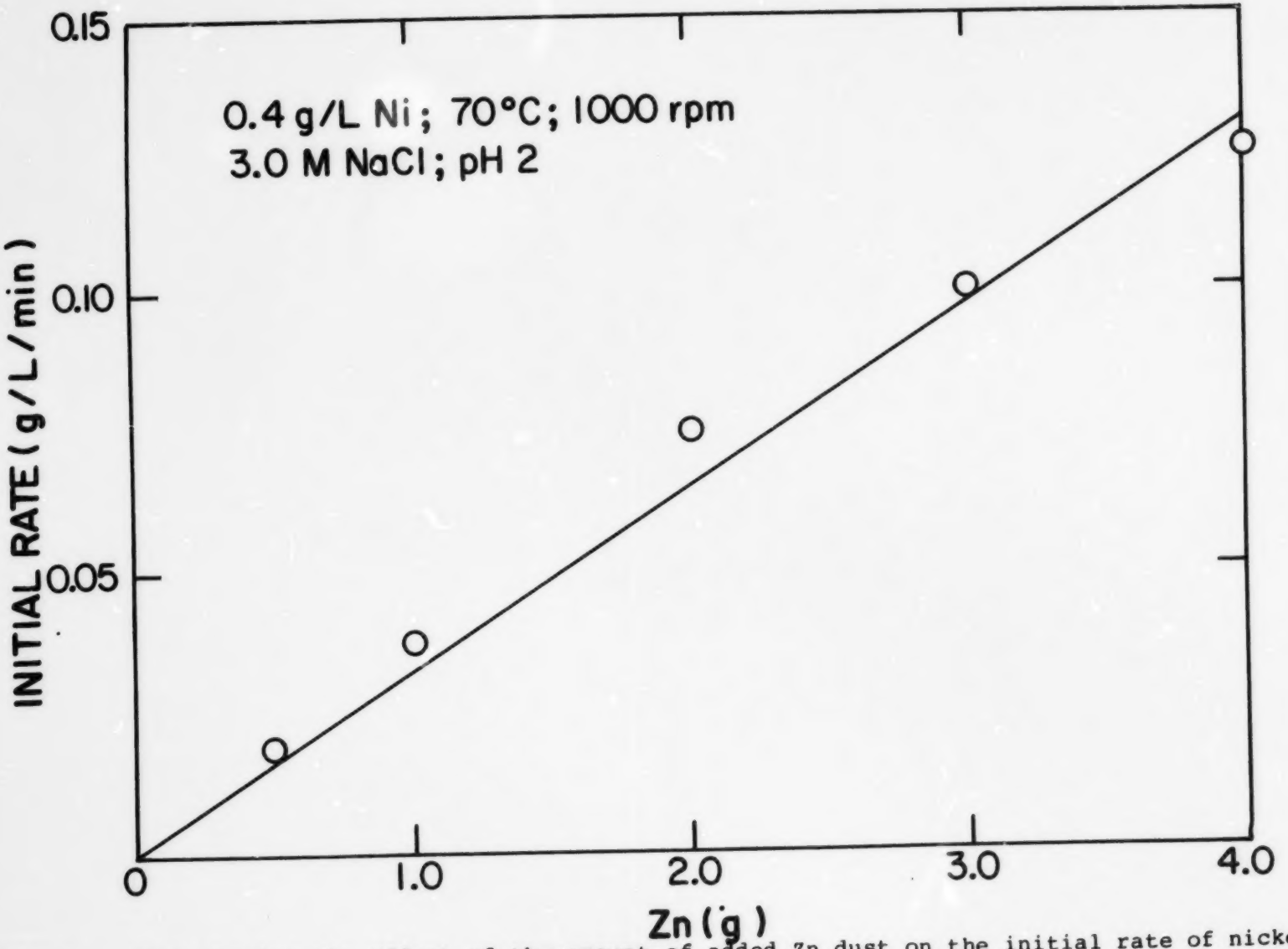

Fig. 5 - Plot showing the effect of the amount of added Zn dust on the initial rate of nickel cementation from 3.0 M NaCl solution at pH 2

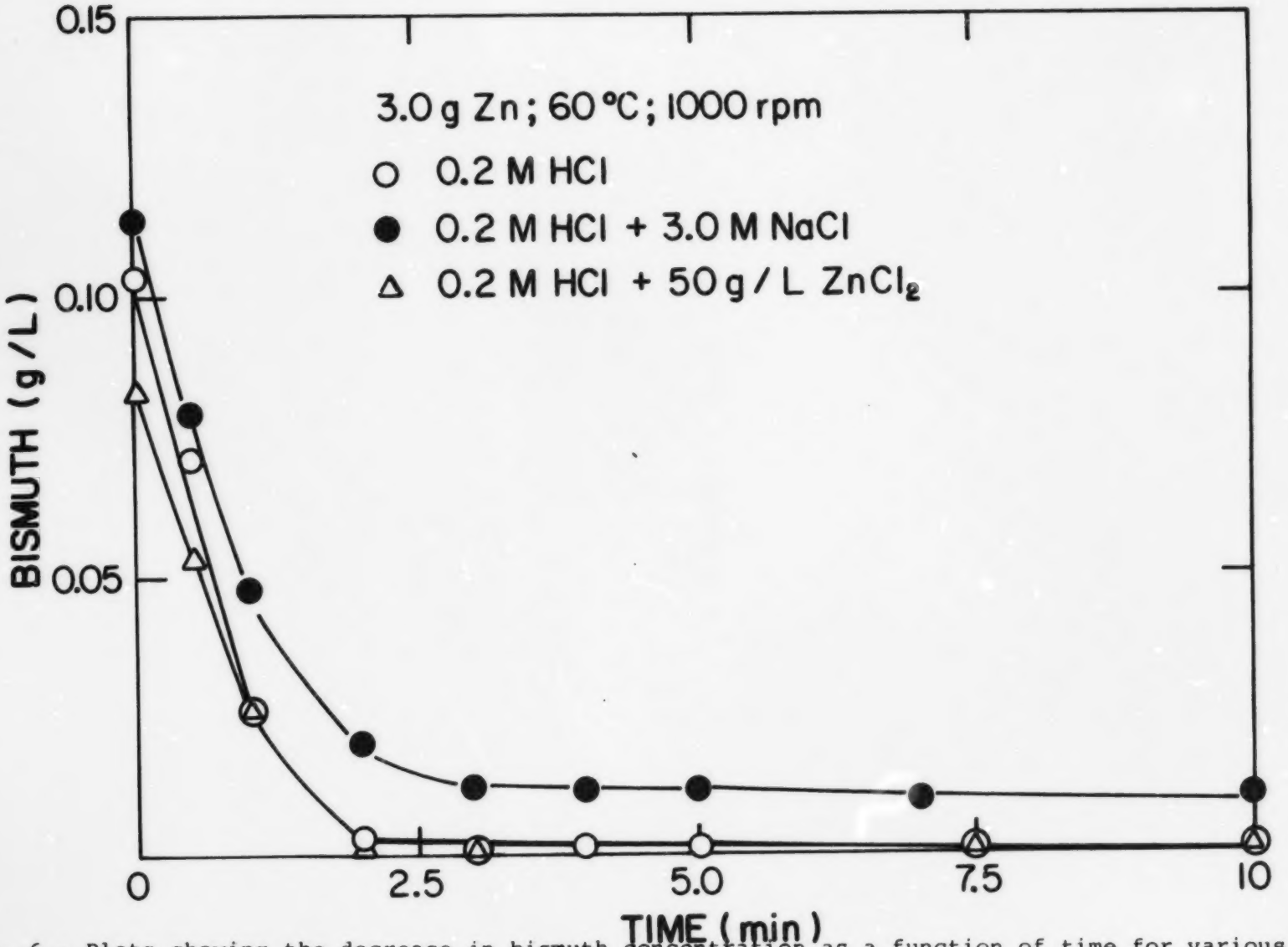

Fig. 6 - Plots showing the decrease in bismuth concentration as a function of time for various chloride solutions.

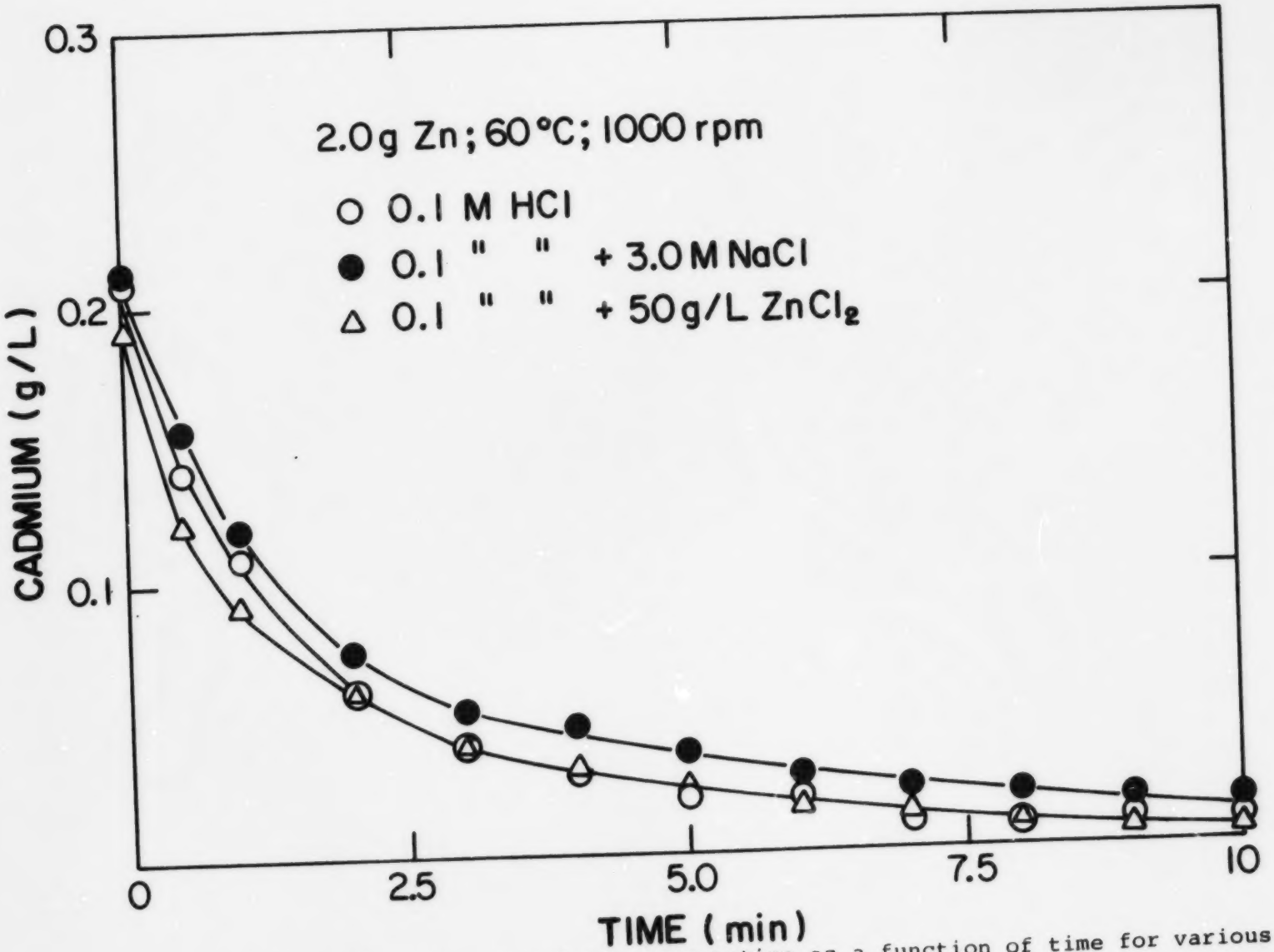

Fig. 7 - Plots showing the decrease in cadmium cementation as a function of time for various chloride solutions.

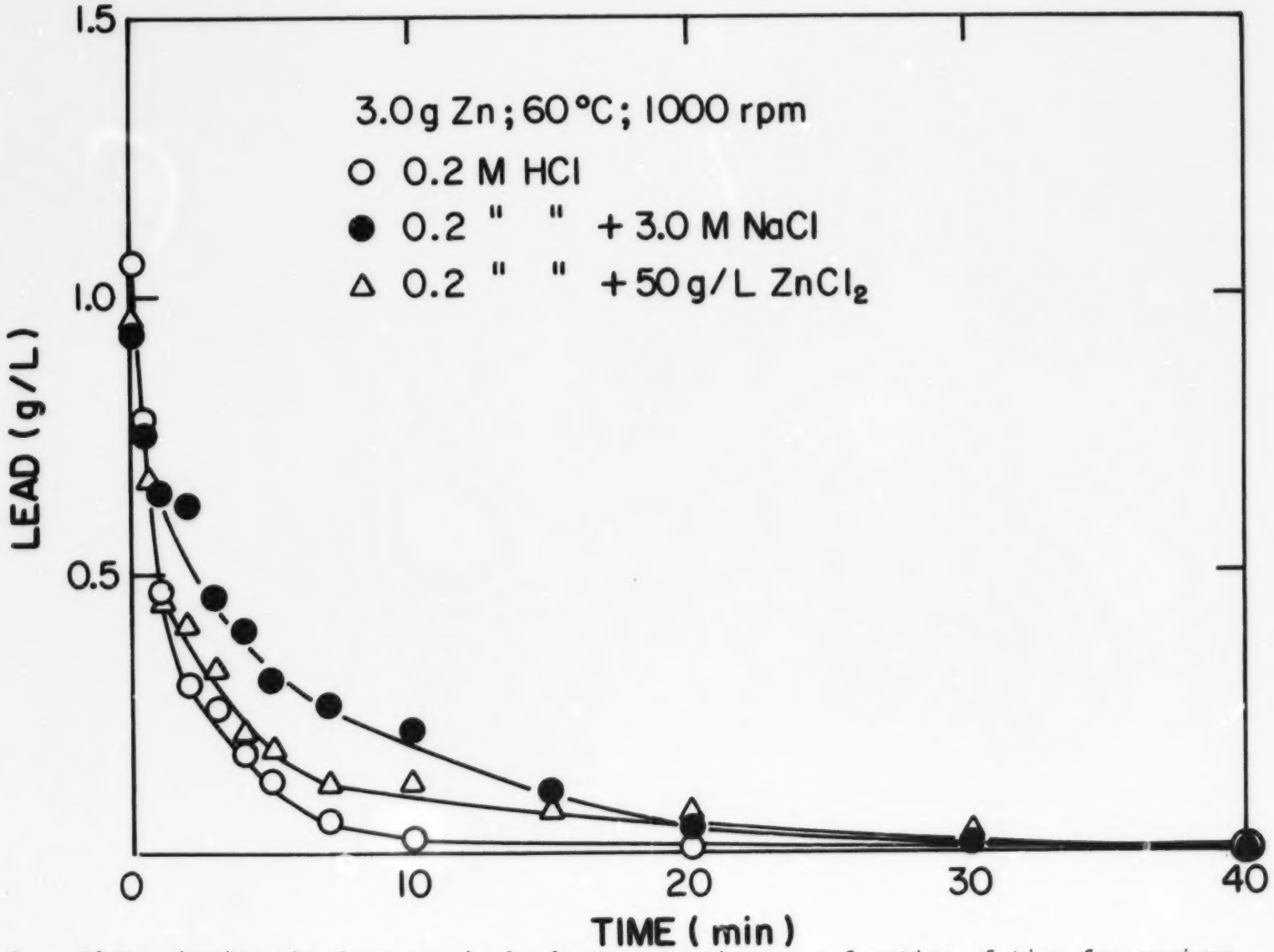

Fig. 8 - Plots showing the decrease in lead concentration as a function of time for various chloride solutions.

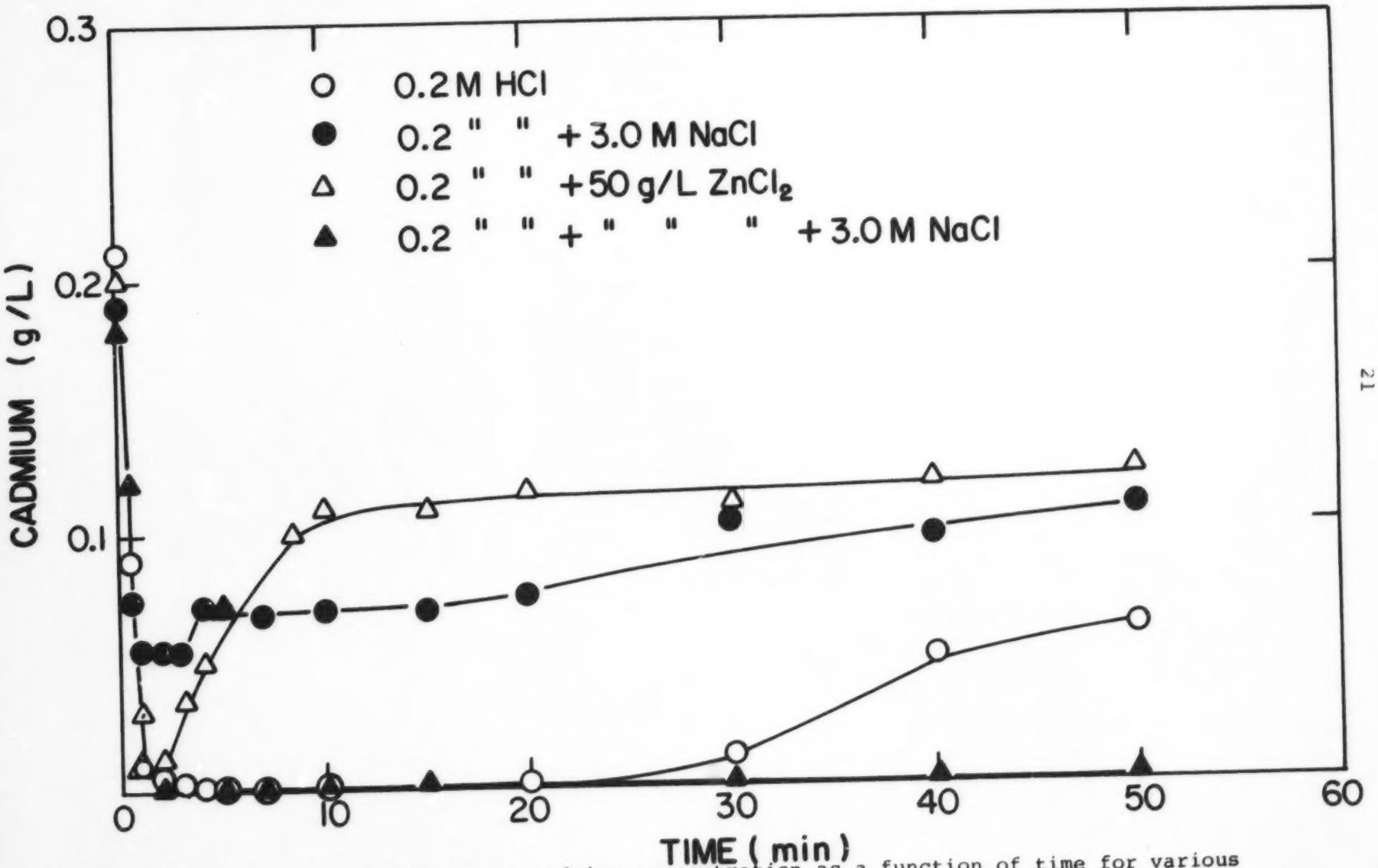

Fig. 9 - Plots showing the change in cadmium concentration as a function of time for various chloride solutions containing the combined impurities.

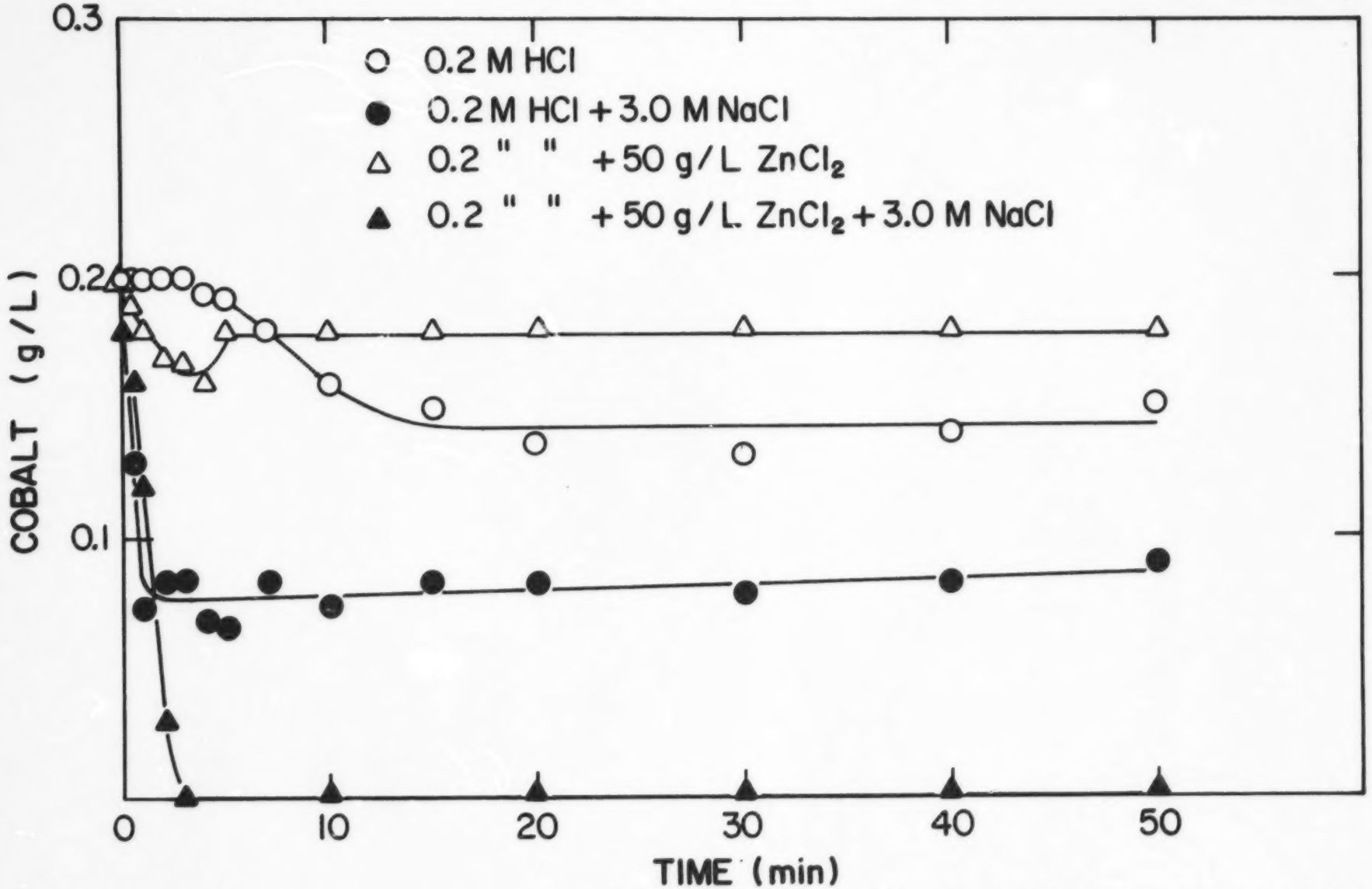

Fig. 10 - Plots showing the change in cobalt concentration as a function of time for various chloride solutions containing the combined impurities.